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Structural and electronic inhomogeneity of graphene revealed by Nano-ARPES

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Abstract. Electronic structure describes the distribution of electronic states in reciprocal space, being one of the most fundamental concepts in condensed matter physics, since it determines the electrical, optical and magnetic behaviours of materials. Due to its two-dimensional honeycomb lattice with covalent bonding, pristine graphene exhibits unsurpassed in-plane stiffness and stable structural properties. Here by employing angle-resolved photoemission spectroscopy with spatial resolution $\sim$ 100 nm (Nano-ARPES), we discuss in detail the structural and electronic properties of graphene grown on cooper by chemical vapour deposition (CVD). Our results reveal the spatial inhomogeneity of graphene film, demonstrating the power of Nano-ARPES to detect the microscopic inhomogeneity of electronic structure for different materials.

1. Introduction

Despite its rapid exploration and application, graphene overlayers on metal surfaces still present various phenomena which are far away from the being completely understood[1, 2, 3]. Recently, commercially available cooper foil has become an efficient and inexpensive substrate for scalable growth of large-area graphene films[4, 5]. However, the dramatic variation of graphene quality from case to case implies that the interaction between graphene and Cu can not be simply considered as "weak". This limits the ultimate application of massively produced graphene and raises the inevitable requirement of highly precise electronic structure description.

Although high resolution angle-resolved photoemission spectroscopy (ARPES) has been well established as a powerful technique to probe distinctly the electronic structure of complex materials[6, 7], conventional ARPES has its limitation to describe the impact of the polycrystalline nature on the low energy quasiparticle behaviour of graphene films on copper foils[8, 9]. Here we employ the first ARPES facility with spatial resolution down to sub-micrometer scale (Nano-ARPES or *k-microscope*)[10, 11] to study the graphene grown on Cu

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foil at both macroscopic and microscopic scales. We will show the phase complexity of graphene overlayer on Cu substrate. This conclusion may stimulate further interest to explore more novel graphene phases based on transition metal substrates.

2. Experimental details

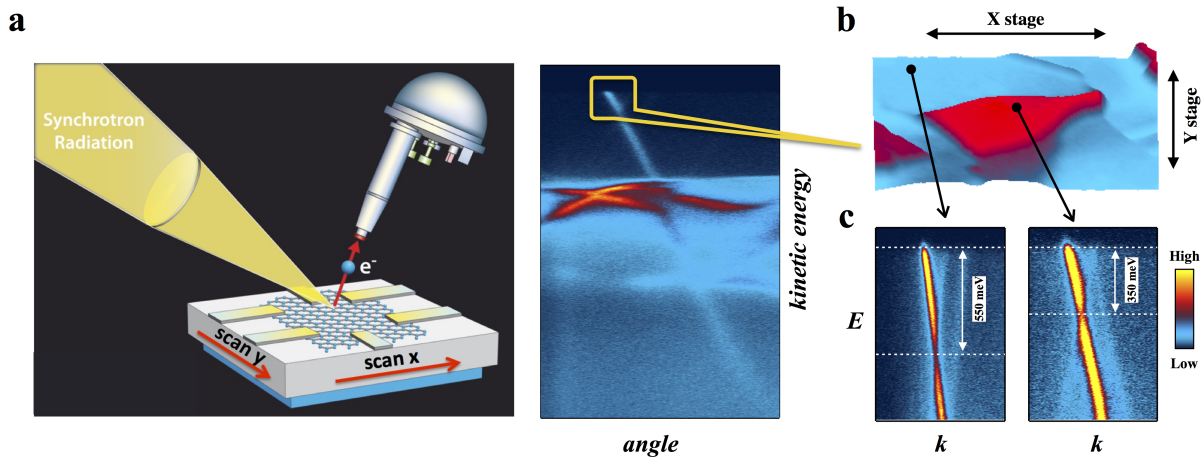

Figure 1. a, Working principle of Nano-ARPES. **b,** Graphene Dirac cone spectra intensity distribution image and spatially resolved Dirac cone detailed structure.

To begin with, the working principle of Nano-ARPES is illustrated in Fig. 1a. Fresnel zone plate is used to focus the synchrotron radiation beam into nanometer size. The sample is mounted on a high-precision scanning stage with five degrees of freedom. Piezoscanners allow zero backlash and nanometric accuracy in the linear motion. Interferometers are used to control the simultaneous movement of sample and zone plate. Images of the sample chemical composition and angle-resolved valence-band states can be obtained by synchronized scanning of the sample and collecting the photoelectron by energy analyzer.

As shown in Fig .1b, the spectra intensity distribution image of graphene upper Dirac cone was generated by integrating the corresponding energy-angle window and scan the sample along two in-plane axises. The variation of spectra intensity clearly illustrates the electronic inhomogeneity of graphene on Cu. From any position within the scanning range we can extract or remeasure the detailed electronic structure. As shown the Fig. 1c, the inhomogeneity shown in the image indeed comes from the electronic phase separation. The Dirac cone shown in the left panel, with weak upper Dirac cone intensity actually is highly doped, with the Dirac level lying 550 meV below the Fermi level. For the Dirac cone shown in the right panel with strong intensity, the doping level is 350 meV. This clear contrast not only demonstrates the ability of Nano-ARPES to detect the microscopic electronic inhomogeneity, but also reveal the complexity of seeming simple structure of CVD graphene on Cu.

3. Macroscopic electronic structure of graphene on cooper

The optical image shown in Fig. 2a highlights one particular Cu grain with different contrast (top middle) compared with the surrounding ones. The spatial resolved-capability of Nano-ARPES allow us to locate this grains from the intensity distribution image of Dirac cone (Fig. 2b). The Fermi surface, mapped in normal ARPES mode with spatial resolution $\sim 50\ \mu$m, is shown in Fig. 2c. It is clear that graphene in this area has multiple orientations while one orientation indicated by the red hexagon is dominating. From the Fermi surface we can also see

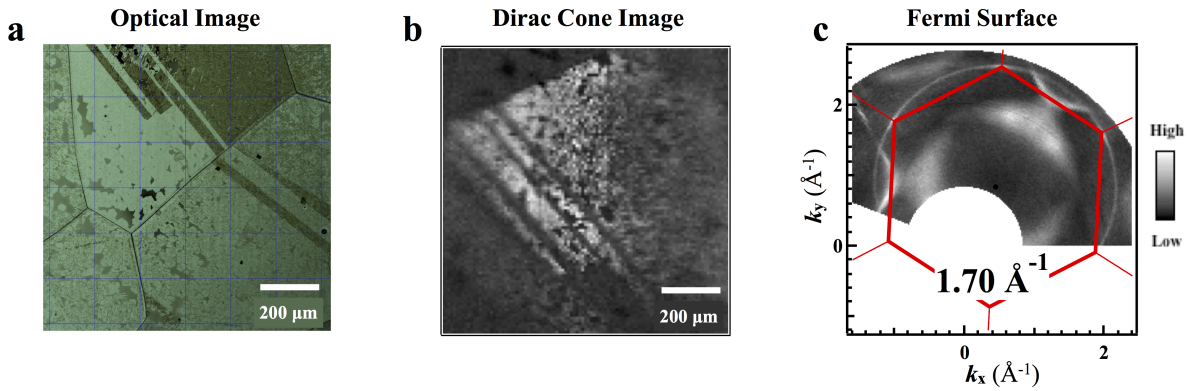

Figure 2. **a,** Optical image of Gr/Cu. **b,** Nano-ARPES real space image of the Dirac cone intensity distribution. Scale bar 200 μm. **c,** Fermi surface of graphene grown on Cu (111) from the same area as shown in **a** and **b**.

the part from Cu *sp* bands, of which the hexagonal symmetry helps us to define that, for this grain, graphene is covering Cu (111) surface. These information gives us the general picture of

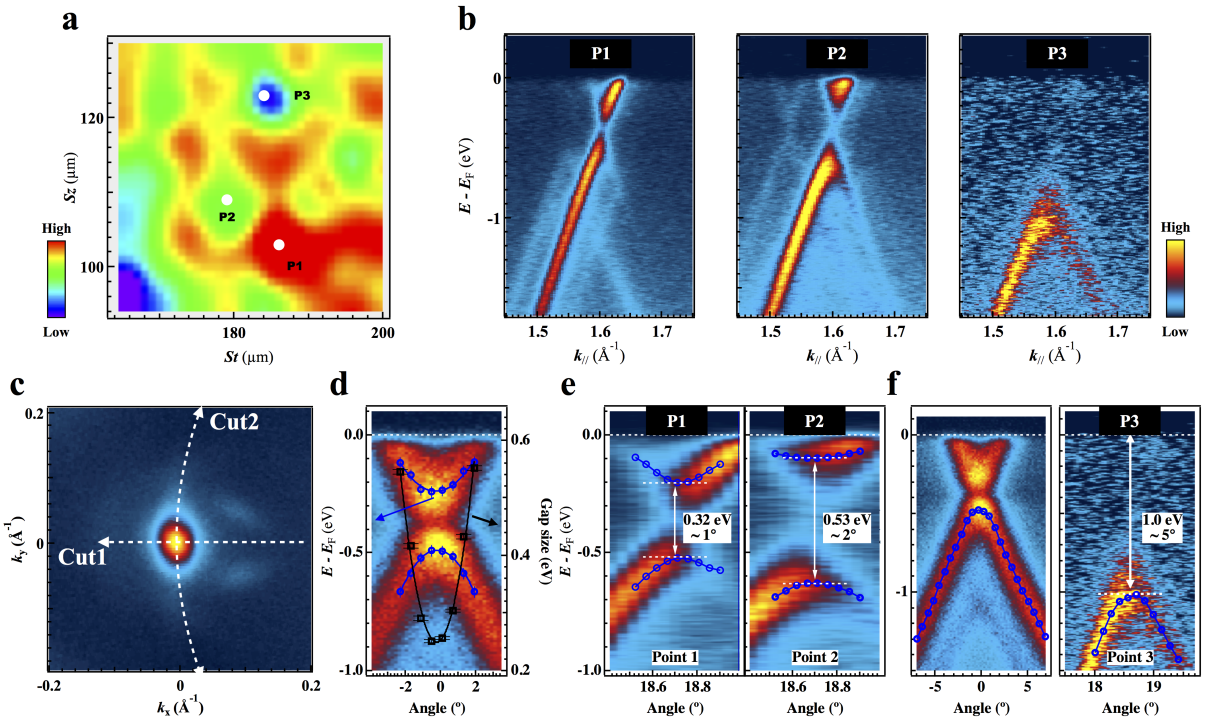

Figure 3. **a,** Dirac cone intensity distribution image. **b,** Detailed electronic structure of graphene Dirac cone corresponding to different points shown in **a**. **c**, Constant energy (Dirac energy) contour for Dirac cone of graphene. **d,** Dispersions extracted from Cut2 shown in **c**. **e,** Detailed analysis of the dispersions shown in **b**. **f,** Left: dispersion extracted from Cut2 shown in **c**. Right: detailed analysis for dispersion from **P3**. Cut1 represent the direction where dispersions shown in **b, e** and right panle of **f** are along.

the sample being studied, allowing further detailed analysis as will be shown in the following.

4. Microscopic electronic structure of graphene on cooper

we now turn to discuss microscopic rotational domains in this area. Fig. 3a shows the upper Dirac cone intensity image in microscopic scale. From the Dirac cone spectra from different positions shown in Fig. 3b, it is clear that the contrast shown in intensity image comes from the orientation change of the graphene. That is to say, while for **P1**, the dispersion is taken across the K point within $\pm 1\ ^o$ accuracy, for **P2** and **P3**, the dispersion cut is slightly away from K point. As the measurement plane is fixed for photoemission process, this angle difference means that graphene in **P2** and **P3** is rotated respect to **P1**.

As analysed in Fig. 3d, by fitting the upper and lower Dirac cone bands along *KK'* direction (Cut2), we obtain the relation between the gap size and rotation angle, indicated by the black curve. From this relation, we can determine the relative rotation angle to be ~ 2 and $5\ ^o$ for **P2** and **P3** respectively. In reference[12], we prove that the graphene lattice structure changes dramatically with respect to the rotational angle, due to the interaction with the underlying Cu. Here, by microscopically show the existence of several rotational domains , we may expect very different structural behaviour for graphene.

By exploring the electronic structure of graphene on copper foil from both macroscopic and microscopic scale, we demonstrated the phase complexity of CVD graphene on Cu (111). Detailed Nano-ARPES analysis shows the existence of graphene domains with different rotational angle and possible structural change, deserving further detailed exploration by advanced tools such as Nano-ARPES, microRaman, STM and so on.

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